Investigation of Contamination Effects on Laser Induced Optical Damage in Space Flight Lasers

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Abstract:

Molecular and particulate contamination within laser systems represent two of the largest risks associated with laser systems. Optical design typically minimizes the risk due to strictly optical intensity damage related issues. However, the presence of contamination in the laser system can negate the designed in safety margins, resulting in optical damage under conditions where it would not normally occur. NASA has adopted risk management as a universal goal, to manage risk, one must know what it is. This requires a fundamental understanding of the principle processes.

There have been about ten papers published in the area of molecular contamination induced laser optical damage.[1-14] These papers have primarily been investigations into single events and have not provided significant insight into the behavior that can be expected in other cases. This is expected, as the current state of laser induced optical damage is not understood at the materials level. Without the knowledge of the changes in the optical materials during laser damage events, understanding the contributions of outside materials in combination with the optical materials is beyond hope.

This project investigated the contamination effects on the laser optical damage process both at a theoretical level and through laboratory measurements. A numerical modeling paradigm has been developed for the interaction of laser beam intensity and matter at the atomic and molecular level. Measurements have been made that provide heretofore-unseen behavior in laser optics that provides significant insight into the behavior of laser damaged optics.

I. Introduction

Laser based instrumentation and communication systems provide capabilities that are otherwise unavailable. Since the first corner cube was placed on the moon, to allow the tracking of the distance to the moon, the capabilities of laser based space measurements have held the promise of providing information that would be otherwise impossible to obtain. Laser altimeters such as the Mars Orbiting Laser Altimeter (MOLA) can provide detailed high resolution altimetry of distant planets. Differential absorption LIDAR systems can provide spatially resolved spectral information about the atmosphere and the environment allowing a wide variety of information to be recovered i.e. algal growth in the oceans, gain and loss of ice packs, vegetation canopy height and density, etc.

A. Spaceflight Laser System Challenges

There is a downside. The construction of a space flight capable LIDAR system is far from simple. The space environment and mission requirements for these systems are extreme. Building a one joule per pulse laboratory laser while not being a simple matter, is far from as difficult as building one for space flight use.

Very few earth based lasers are required to operate in a vacuum, with no physical connection outside the uptake and loss of energy radiatively. The additional requirement that the laser survive and remain aligned after shaking, being accelerated at fifteen times gravity, thermal cycling and having the external pressure change by an atmosphere further complicate the issues.

In addition, as earthlings, we do not normally work in ultra high vacuum environments, and so, our knowledge of material system behavior in the vacuum of space is limited. The effects of placing a piece of hardware in a space like environment results in a number of widely varying conditions for the materials in the system. The composition of the surfaces and the transport of material that out gases from the hardware changes dramatically. In addition, the time dependence of these behaviors is not well known.

The cost of launching a piece of hardware into orbit is high. The cost is often scaled on a by weight basis. The result is that the hardware must be scoped such that the launch mass is minimized. Power is likewise at a premium, both in usage and dissipation. There is only a certain quantity of energy that may be captured with reasonable size solar arrays, and conversely there is a limit on the amount of waste heat that can be rejected by radiator panels. These constraints result in a great emphasis on the miniaturization and the efficiency of the systems. Thus, systems are operated at near materials limits for power and mechanical strength. This results in the ingress of behaviors that are normally not dealt with due to the pushing of limits of what is known about material behavior.

Therefore, in space based laser systems, it is typical to attempt to push the energy density to near the limits. This can in many cases, especially at high energy densities and long mission lifetimes result in issues that have not yet been

seen, or are poorly understood. These are the issues with spaceflight lasers.

The typical spaceflight lidar system operates in the ten millijoule to one joule per pulse regime. These are q-switched systems with pulse lengths typically in the one to twenty nanosecond range. Within these systems, the energy densities generally run in the 100 to 500 million watts per square centimeter range for two millimeter to ten millimeter beam waists. These energy densities and pulse lengths place the demands on the optical materials of these systems on par with systems such as The National Ignition Facility, (U.S.A.), Laser Megajoule (France), etc. In addition, mission lifetimes are measured in millions to billions of shots. These shot counts are much higher than typically seen between service intervals in most laboratory lasers, and well beyond the expected lifetimes of the large facilities. So, slight changes seen in the much larger lasers that define optic lifetimes, can result in much greater changes during the lifetimes of spaceflight systems.

Laser optical damage is typically an issue of a lower tail probability event. The lasers are designed so that based upon the knowledge of the mean behavior of the system, they do not damage on the first laser firing, or within some predetermined number of laser operation cycles. The issue becomes when dealing with millions to billions of events, one damage event is catastrophic. Thus, the mechanism of the damage and any changes in the system must be known. This is typically not the case. Description of the mean or average behavior is inadequate to describe the anomalous behavior. To understand the anomalous behavior it is necessary to have the capability to address microscopic materials behavior and its effect on the total system. Electronic quantum chemical modeling allows this and was originally developed to address spectroscopic behavior that was originally undescribable by other techniques.

B. Contamination Effects

Contamination is a particularly complex issue. Typical contamination effects result in the slow degradation of the performance of some aspect of a system. Ground based systems, although contamination sensitive, are typically less contamination sensitive than spaceflight systems. In ground based systems, there is typically some option available for mitigation of the contamination effects either through repair or replacement. In space, the issue of repair or replacement becomes much more difficult if possible at all. Further, because of the radiation environment, and the lack of oxygen, the behavior of contaminants is different. Hydrocarbons and plasticizers, which typically just scatter light in earth like environments, will turn black and absorb a significant amount, if not all of the light in an optical system.

The paradigm of high intensity laser optical damage is in conditions where the behavior is not described by linear optical properties. In this regime, the issue of laser damage is largely that of what might otherwise be called anomalous laser damaging behavior. This includes damage precipitated by particulates at or near the diffraction limit. Damage that results from changes in the behavior of an optic due to some time dependent laser induced effect. With regard to contamination, it principly involves the damage induced by contamination significantly less than a wavelength in thickness, and typically involving a material that would be predicted to have an absorption significantly less than 10^{-6} cm^{-1}. Under normal conditions, following normal physical behaviors, there would be no induction of laser damage. But, damage ensues under these conditions time and time again. The Laser Induced Optical Damage in High Intensity Lasers Symposium is currently in its 36th year, studying these very issues. There are currently more questions than answers.

Laser damage behavior changes dramatically with changes in the laser system. Laser induced damages thresholds, LIDT's, are the statistical values for a series of optics, at which damage probabilities become significant. Current treatments of LIDT vary significantly with wavelength, pulse length, pulse height, beam diameter, mode structure, and peak energies. There are a number of empirical relationships that are applied to relate the behaviors within each laser behavior regime, but they are sufficiently variable to negate relationships between more than one variable.[15] In addition, it is known that under vacuum or inert purge conditions that the risk of molecular contamination related damage increases over systems operating in air.[2,10]

In the case of contamination in vacuum ultraviolet laser lithography, the laser induced contamination follows a linear behavior with respect to total flux.[14] This case is unique in that one of the main sources of molecular contamination is the lithography mask. The mask has a large photon capture cross section, and is made of organic polymer. The photon energy of the incident laser is at or above the ionization energy for the mask polymer. In addition, the ultraviolet laser pulse energy is significantly below the intensities used in spaceflight instruments and other q-switched lasers. Thus, the behavior is strictly first order. The mask material has a capture efficiency of effectively one for the incident photons. There is a given quantum efficiency for the photolysis of the mask, and an effectively constant capture efficiency for the photolyzed species on the optics in the vicinity of the mask. These are not the same conditions or environment as seen in higher intensity or longer wavelength systems, and thus are not applicable.

C. Spaceflight Laser Contamination Effects

In spaceflight lasers the effects of contamination are amplified greatly. Due to the intensity of the laser beam, the effect is not to just deposit material on the surface of the optic, the laser subsequently causes the optic to break. This results in the catastrophic loss of laser function. The

threshold for contamination in a laboratory laser is typically much higher than in a space like environment.

Due to the size, efficiency, and pulse energy requirements for spaceflight laser systems, most if not all of the systems will fit into the high energy pulsed laser regime. Within this regime, the behavior of materials is not well understood. It can not be assumed that the description of a material by a normal laboratory spectrometer will be adequate. Laboratory spectrometers are specifically designed to operate at very low intensities. This was done to minimize the effect of high light intensities on the material in question. It is much simpler to install a larger light source than to create a much more sensitive detector.

In sealed or vacuum laser systems, it is common to find time dependent contamination behavior. The laser will operate under what is presumably constant conditions for some time frame the precipitously degrade either in a rapid drop off or a single catastrophic event. There is currently not a good understanding of this behavior, but it is recognized as being expectable. The laser contamination behavior while in many cases is expectable, is not predictable.

II. Common damaging contaminants

There are some materials that are known to be cause damage in laser systems. These contaminants fall into two general descriptions, particulate and molecular contaminants. Molecular contaminants are typically considered to be materials that lack a distinct solid shape and transport either due to gas phase transport or other molecular transport methods. Particulates are described as those materials that are typically transported due to more physical transport mechanisms such as falling or being carried suspended in a gas. Molecular contamination can be carried by the same physical processes as particulates, but are not limited to such transport. There are bad actors and not so bad actors in each case, and the behaviors are dependent upon the conditions.

Metallic particles and refractory solids are known to be bad actors as they will absorb radiation efficiently, and result in the formation of plasmas as they absorb energy with sufficient efficiency to heat to their point of vaporization and/or ionization. The resultant plasma explosion, or thermal damage combined with the initial perturbation of the laser diffractively can propagate damage throughout the laser. Metallic particles can form mirrors in inopportune locations, causing internal focusing of the laser, or modification of the base optical materials, inducing strong absorptions of the laser energy, resulting in the deposition of large amounts of energy in the surface of the optic. Refractory particles such as carbon, and inorganic oxides can result in the point heating of the surface of the optic resulting in permanent thermal distortion or stress fracture.

Molecular contamination effects are more convoluted. The interaction of the molecular contamination with the laser beam varies more significantly and is less well defined than that of particulate contamination. Primarily, the molecular contamination of most interest is that which occurs between molecular contaminants that are expected to be nearly transparent in the region of interest. Two examples of molecular contaminants that are bad actors are silicones and aromatic hydrocarbons such as toluene. Both of these materials are essentially transparent throughout the near infrared and visible range. These materials do not possess sufficient absorption of energy for thermal changes to occur. Yet, both of these materials are known to damage laser optics in one micron lasers.[1,2,4,11] Again, both silicones and aromatic hydrocarbons are at times worse than at other times.

III. Conditional effects

As stated in the preceding paragraphs, there is objective evidence that contaminants behave differently under different conditions.[2] This is not unexpected, as all materials behave differently under different conditions. Contamination related laser optic damage is primarily a surface phenomenon, with the exception of particle induced diffraction effects. Thus, the surface composition within the laser at the time of the laser damage event is critical. This includes such species as ubiquitous water. Water, like other species normally ignored due to their ubiquitous nature, significantly changes the surface energy and thus the behavior of a surface. The surface adsorption energy of the water decreases the surface energy of the surface upon which it is adsorbed.

In the discussion of the surface composition, it is not adequate to assume that the average composition of the bulk will be the composition of the surface. The surface differs greatly from the bulk. Although the elemental composition may be the same, the energy and the local fields differ significantly. On one side of the surface, there is the bulk of the material. On the other side there is not. This results in the net sum of the forces of the bulk adding up in one direction, and in the other direction not. This results in a very large force field at the surface.

Adamson in discussing the magnitude of the surface energy, states that the surface energy/surface pressure at zero Kelvin is the energy required to break the material at zero Kelvin.[16] Thus, in the absence of movement of defects or dislocations, the surface energy is the tensile strength in the absence of other fracture mechanisms. The actual surface energy may exceed the tensile strength by one or more orders of magnitude. For materials such as silica and other optical materials, this is a huge number. The apparent surface energy is reduced significantly by the adsorption of water and other materials on the surface.

The adsorption of materials on a surface lowers the net energy of the material being absorbed and the surface upon

which it is being absorbed. Within the earth's atmosphere, there are few if any pristine surfaces. Most surfaces are covered with ten to fifty atoms deep of surface adsorbed water. This becomes immediately apparent when placing items in a high vacuum system. The residual gas load of such a material will tax even the fastest of vacuum pumps and result in higher than normal pressures until baked out.

Ultra high vacuum systems, which attempt to obtain space-like vacuum, are typically unable to reach this vacuum level without very high temperature long duration bakeouts. The reason for this behavior is the surface adsorbed water. Surface adsorbed water forms a virtual leak, or continuous gas load. It is estimated that the time required to remove all of the surface water from an ultra high vacuum system at room temperature by pumping at room temperature is on the order of one thousand years. This is value important on several levels.

As the vapor pressure of water at room temperature is about seven Torr, a first approximation says that the water should be gone when the pressure is below seven Torr. This is erroneous as water is the highest concentration material in most vacuum systems down to about 10^{-11} Torr, where it is typically replaced in the top position by hydrogen. Thus, as water is removed from a surface, it becomes more difficult to remove the water. This is due to Van Der Waals(or London) forces. Therefore, the cleaner the surface is the higher the energy of the surface.

It is known that radiation of the surface within a high vacuum system will desorb the surface bound water. Special ultraviolet lamp systems are sold for this purpose. In addition to the dislodging of the water from the surface, the ultraviolet light can provide sufficient energy to photolyze the water to extremely reactive species such as ozone and hydroxyl radical. Likewise, multiple photon processes will act in a similar manner activating and dislodging water.

It is also worth noting that the purification of water to remove all residual organic materials is carried out using high pressure mercury arc lamps. These lamps generate ozone from the dissolved oxygen in the water and hydroxyl radical from the water photolysis. These systems provide water virtually devoid of any organic contaminants. The organic contaminants are oxidized and consumed in the water.

IV. Non-linear optical behavior

Non-linear optical behavior, like non-linearity in mechanical oscillator systems is not adequately described in undergraduate curricula. A typical discussion of hyperpolarizability (a key behavior in non-linear optical behavior) goes something like this, “hyperpolarizability occurs in laser systems, as a result we will not discuss it further.” Elsewhere the text goes into a discussion of Raman spectroscopy, a non-linear optical property, based upon hyperpolarizability.

The classical harmonic oscillator equation, as applied to springs, beams, molecules, etc. is a special case of the anharmonic oscillator. The harmonic oscillator is described by $F=kx$. The anharmonic oscillator is described by $F=k_1x-k_2x^2+k_3x^3-k_4x^4+k_5x^5....$ The special case of the harmonic oscillator is where the potential on both sides of the null point at all distances is equal. If the potential of the oscillator varies from one side to the other, the Fourier analysis of the perturbed function generates a wealth of harmonics. In the case of molecular behavior, the oscillator potential, as simply modeled by a Morse potential, is inherently non-linear.

As a general rule, the odd harmonics are allowed in all cases. The even order harmonics require a lack of central symmetry. The odd harmonics will be present to varying degrees at all time. The even harmonics will be ever present at surfaces as the surface is different on each side, in one environment on one side, in a different material on the other. Even order harmonics can be generated through two frequency addition, thus the third harmonic minus the first harmonic yields the second harmonic. This is the most probable mode of formation of second harmonics.

Non-linear optical effects behave in the exact same manner. The various non-linear behaviors are mixtures of the anharmonic oscillations in three dimensions. The optical anharmonic oscillator potentials are functions of the time and directional electronic potential gradients within a material. The electronic potential gradients are dependent primarily upon the interatomic forces in the material. As all forces acting upon a material affect the electronic distribution and thus the electronic potential gradients. In addition, point defects, inclusions, and interstitial materials affect the potential gradients within the material.

The magnitude of intermolecular forces is on the order of 10^{10} volts per meter. In high intensity laser systems, the electric field approaches or exceeds this field intensity. Thus, the effective electric field of a laser is significant with respect to the intermolecular forces. Thus, the deviation of the behavior of an oscillator in the presence of a laser electric field results in a significant change in the properties of the material.

The presence of a point defect within a material will generate a distortion of the electric field within the material. This distortion in the presence of an imposed field will further distort the field at the point. Further, the distortion of the electric field at the defect will distort the electric field in the surrounding matter. This distortion will further distort the point defect. This will continue to propagate at a rate dependent upon the directional index of refraction of the material, for the duration of the laser pulse, in a time dependent manner. Within a piece of matter, the net

distortion of the electronic potential gradients will expand within the duration of the laser pulse, and be affected by thermal, mechanical, electric and compositional gradients in a time and field dependent manner. The size of the initial defect will have some effect upon the rate and extent of the distortion.

The increase in the distortion of the electronic potential gradients results in an increase the non-linear optical properties. The distortion of the electronic distribution will change any symmetry relationships that might have previously prevented non-linear activity. Thus, changing from a centrosymmetric system to a system with zero distortion from symmetry to a macroscopic asymmetry, will result in a multiplier changing from zero to a non-zero value. This results in a significant shift in behavior.

The distortion of the electronic distribution is precisely the induced polarizability and hyperpolarizability of the system. The total polarizability (polarizability and hyperpolarizability) determines the interaction of the system with light. The rudimentary source of the polarizability or total polarizability is the net dipole moment and the higher net multipole moments, which are affected by the molecular environment. These result in changes in the electronic and thus optical behavior of the molecular system. These necessarily increase the intensities of the higher order harmonics in the system. The time dependent sum of the distorted electric fields directly add to the net time dependent field on the electrons, driving the non-linearity.

These changes in the electronic behavior will accentuate the harmonic generation and other non-linear behavior. The amplification of the higher harmonics in an optical system will lead to more ultraviolet and higher energy radiation generation. The increase in the ultraviolet radiation will functionally decrease the amount of water present on the surface of the optic. In addition, this increase in the ultraviolet radiation will drive the formation of ozone and hydroxyl radical resulting in the consumption of organic material at the surface until the water is consumed, or the kinetics of the replacement of the water and oxygen is exceeded. At this point the photolysis of contaminants on the surface of the optics will occur. The photolysis in the absence of oxidizing species will result in the deposition of highly carbonaceous deposits. Under the conditions of moderate vacuum to air, the carbonaceous deposits will be oxidized. Silicone under these conditions will deposit silica due to the oxidation of the silicone.

With the increase of the effective ultraviolet radiation density due to multiple photon absorption and non-linear scattering, population of excited states will occur. Excited state species will be more strongly attracted to surfaces.[17] This stronger attraction results in greater distortion of the polarizabilities, increasing the adsorption energy and the optical absorptivity.

V. Quantization

It is not widely acknowledged that the quantization of energy states defines the “stable” energy states. This means that the energy states have some macroscopic lifetime. The interaction or scattering of photons that results in the index of refraction, requires that the energy of the light be present within the matter. The indices of refraction, are known to be defined at all wavelengths, the functions are continuous. These indices contain real and imaginary components. The imaginary components result in the absorption of light. At any wavelength where the refractivity is not precisely zero, or conversely the index of refraction is not precisely one, the matter interacts with the light. Thus, where the refractivity is not zero, the absorption of light, or the interaction of light with matter is feasible.

In the condensed state, the local fields within the matter will perturb the energy states of matter, resulting in the smearing of energy states. Therefore, while the interaction lifetimes may be short, there is interaction never the less. This requires the material to be capable of sustaining the energy of the incident radiation through the distortion of the polarization of the matter. [18]

In cases of limited, near zero refractivity, and near zero absorptivity, the lifetimes of the interaction of the energy of the photons with the matter are limited. Therefore, the probability of an interconversion(mixing) of the energy from one energy state with another is limited. If the lifetime of the excited state interaction, is sufficiently extended, the probability of an interconversion will rise. Thus, stabilization of an excited state through internal conversion or other method, will increase the lifetime of the excited state, and thus the probability of relaxation through a route not emitting the same amount of energy (same photon energy). With the increased excited state lifetime in a polarized state, the probability of a multiple photon event will likewise increase. [19]

It is probable that at the time of the development of quantum theory the concept of photon arrival rates and multiple photon events were not significantly considered. Likewise, the concept of photon arrival rates exceeding the kinetic rate of photon emission were likely not considered, except as an anomaly. With the advent of high energy pulsed lasers, it is not uncommon for these effects to be in operation. Further, it is reasonable to expect that with short laser pulses, that the perturbation of the material behavior during a laser pulse could result in a significant change in the absorptivities and emissivities of materials to change in sufficiently short time periods to trap energy in a material. Thus, with the beam on the material can absorb energy faster than it can emit it, and when the beam stops, transition the matter to a state where the the emission is forbidden.

VI. TRAPPED ENERGY

Glassy materials have a long rich history. Glass has been utilized and studied since before the beginning of written history. Its behavior has been well recorded even if not well understood.

Digression 1
As a preface to further description, a short digression is required. Most of our interaction and perception of matter is based upon electrons. It is fair to say that with the exception of mass and nuclear interactions, our universe is described by the behavior of electrons. When you touch something, you are interacting with the electrons. When you see something, you are seeing the effect of the electrons on the light and vice versa. When you smell something, you are sensing the interactions of the polarizability of the vapors in a shape sensitive manner. When you apply a force to something, you are applying the force to the electron distribution around the nuclei. Electronic distributions have many local minima and local maxima. Thus, virtually any force applied to a material, and any stress in a material are stored in the electrons. This said, any potential energy state is an electronic energy state, or can be so represented.

It has been known for an eternity that rapidly heating and cooling glass leads to instability in the piece. This has been ascribed to the freezing in of stresses. The molecular geometry of the atoms in glass is not a stable or equilibrium state. The material will in an infinite time rearrange into the equilibrium crystalline form. The geometry of the atoms in a small volume, in which they are effectively frozen can be described by a fictive temperature. This is the temperature in which they would be in equilibrium. The closer the fictive temperature is to the actual temperature, the lower the stress in the piece of glass. Thus, the difference between the actual temperature of the glass and its fictive temperature is a measure of the distortion, stress and energy stored in the glass. If the fictive temperature is too high, or the gradients in the fictive temperatures is too high the glass will break.

In the past one to two hundred years, it has been determined that high energy radiation will cause changes in the coloration of glass[20,21,22]. This has been described as Farbe center, F-center or color center formation. This occurs in gamma radiation, x-ray radiation, ultraviolet radiation, neutron radiation, proton radiation, electron radiation, and laser radiation. There are numerous descriptions and interpretations of this behavior. It is generally accepted that the behavior is the result of the generation of point defects in the glass. [20]

Within laser optical damage, it has been found that there are changes in the properties of the optical materials. In optics that are exposed to high energy pulsed lasers near the LIDT, regions of densification and rarefaction occur. These result in changes in the optical behavior of the optic in a permanent manner.[21] In other cases, where point laser damage occur, it is often found that subsequent testing of the LIDT, results in lower damage thresholds. These changes result in energy being stored in the stresses within the optical material. This stored energy can be released with the deposition of appropriate energy levels, which promote the material to a viable photo-emission state.[22]

In radiation induced damage to silica, the induced f-centers, with the appropriate application of energy emit light between one and three electron volts. This is one micron to one third micron. The photoemission of radiation damaged silica has been well documented. It has been estimated that the maximum concentration of f-centers is 0.05% of the total silica. [20]

In cases, studied in our laboratories, of one micron laser induced optical damage induced by toluene contamination it was found that over 70% of the silica throughout the entire optic, was at an energy to over three electron volts higher than that of the remainder of the silica (the ground state.) This is shown in figure 1. The lifetime of this state was at least two months, and presumably longer in the dark. This f-center concentration level is over three thousand times that estimated as the maximum by radiation physicists.

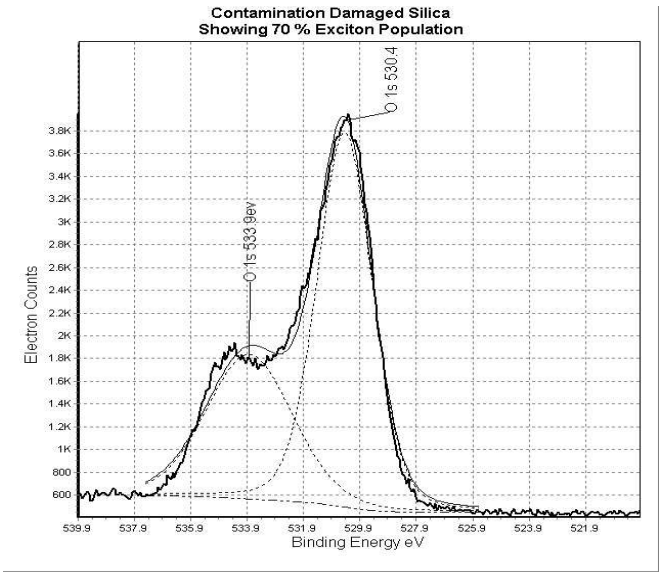

Figure 1 X-ray photoelectron spectrum of oxygen 1s electrons in a contamination related laser damaged optic, showing over 3.5 eV energy differentiation

The energy stored in the damaged laser optic, can be released by zero to three electron volt electrons. Similar energies, as measured by the photoluminescence of laser damaged silica have been measured.[23] The population of the energy levels in the optic have to my knowledge not been measured.

The mechanism of the generation of the population inversion in this case has not yet been resolved. In the case of the surface adsorption of toluene on silica, the electronic orbitals of the toluene will “couple” “overlap” or interact with the orbitals from the silica. This provides a viable route for the population of the energetically elevated silica states. Toluene's first electronic absorption is at approximately 265nm. The wavelength of the fourth harmonic of a 1064 nm Nd:YAG laser is 266nm. This provides a probable route for the population of the four electron volt, 266 nm, four photon or fourth harmonic absorption.

Another potential mechanism is the distortion of the silica by the induced laser field. Following the argument above of the distortion of the absorption profiles and energy states by the laser field, it is possible that the absorption probability of the silica changes sufficiently to allow the non-equilibrium absorption/emission process following either a four photon or fourth harmonic absorption of energy populating the higher energy state.

In the absence of either the laser field, or the toluene absorption, silica, even in the energetically elevated state is transparent at to 300 nm. Thus, the absorption and emission probabilities, following Einstein's equations will be near zero. Therefore, the energy is trapped in a stored energy state. This is exactly the same as the thermal quenching model. And it it exactly the same as the radiation model. The geometry of the atoms in the silica, and the electron densities will shift to provide a metastable state. For thermal stresses, the lifetimes of the stresses is on the order of millenia. With the addition of energy that promotes the energy states from less than one electron volt to a value approaching four electron volts, radiative emission becomes a viable route for relaxation of the energy, and the energy will be released. Thus, the energy stored in the internal stress of the silica is recoverable in a variety of energy levels.

VI. The big pay off

It has been known that some laser optical material such as silica can be laser annealed. Laser annealing is a process in which 355 nm pulsed lasers are fired at increasing intensity levels through silica optics.[15] This energy level is insufficient to normally result in any significant changes in the behavior of silica. Yet, the result of laser annealing is the increase in the LIDT for nearly all laser optics. This phenomenon has been well documented but not understood, until now. The formation of silica results in the formation of stresses within laser optics. These stresses account for energy levels on the order of zero to three electron volts, typically identified as a broad energy distribution of the energies of the silicon and oxygen atoms within the silica. In the presence of the increasing three electron volt radiation of a 355nm pulsed laser, these energies will slowly promote the energies from one to three electron volts to four to seven electron volts. Radiation in the four to seven electron volt range is below the conduction band of silica, but well within the viable emission band of silica. Thus, pumping up the energy allows the material to relax to nearly ground state. This relieves the stresses, and lowers the “ground state” of the silica. This fits all base level descriptions of the behavior of matter, and is consistent with all descriptions of matter. Following Schroedinger's proof “If the model describes the system, the model describes the system.” Therefore it is shown: the model describes the system from the quantum electronic chemical level, describing the system from the bulk to the electronic level.

The population of 70% of silica in a laser damaged optic means that effectively three out of four bonds in silica are at an energy of three electron volts above ground state. The populations and energies of these states were measured using x-ray photoelectron spectroscopy. The maximum distance between elevated energy levels on average is therefore about 3.4 Angstroms (the approximate distance between neighboring silicon atoms in silica.) Meaning, we have potential gradients on the order of one electron volt per Angstrom, or 10^{10} volts per meter. Fields of this magnitude are with the exception of interatomic forces and laser fields, unattainable except in astrophysical environments. This field intensity will result in significant changes in the behavior of the material, causing much greater dielectric response of the matter to incident radiation. This is observed in the laboratory spectrometer measurement of the UV-VIS spectrum of the silica. In addition, this in part explains the changes in the laser optic damage behavior of silica upon the onset of laser damage. The induced perturbation of the silica changes the polarizabilities of the silica, by changing the electron density gradients in the regions of the affected atoms.

The question of the significance of this storage of energy was been pondered by the author for months. Residual stress is stored in glassy material due to either radiation damage, laser damage or rapid quench cooling in the material defects. This energy can be released by the irradiation of the material with a sufficiently high energy (0.1 to 3.5eV.) This energy interacting with the perturbed material will raise the stored energy level to a point at which it will be in a viable emission state, as defined by non-zero Einstein coefficients. Further, this emitted radiation can result in the promotion of neighboring silica molecules that are perturbed, resulting in the emission of their trapped energy, (a form of stimulated emission.)

Digression 2

The formation of matter primarily occurs in stellar fusion events. In the case of silicon, the silicon population will be exceeded by the population of oxygen and other atoms. Consider a silicon atom ejected from the star. As the silicon has been formed at or near the core of the star, it is at extremely high energy. As the high energy silicon atom leaves the star, it travels in the presence of other species,

emitting some energy as atomic emission lines. Along the trajectory of one silicon atom, there will be numerous interactions with other atoms and eventually molecules. Based solely upon population, silicon will react with oxygen. The reaction of oxygen with the silicon will result in the formation of a silica molecule at even higher energy, due to the chemical reaction energy. The high energy silica molecule will then coalesce with other molecules. (This behavior is based upon the description of particle size energetics known as the Kelvin effect, and by fundamental quantum mechanics based upon orbital curvature. Based upon general population densities and chemical stabilities, the probability of forming stable silica and silicates is highly favored. As the coalescence occurs nearly totally immersed in a radiative heat sink of seven Kelvin, the particle will radiatively quench cool quickly. The radiative heat transfer is controlled by the difference between the source and the sink temperatures to the fourth power. It is therefore quite reasonable to describe interstellar dust particles as quench cooled or thermally stressed. The additional astrophysical magnitude stresses imparted on the particles being ejected from a star will additionally perturb the particles. Thus, it would be reasonable to assume that interstellar dust will have relatively high fictive temperatures or stresses, and be populated with f-centers and other point defects.

Within the astrophysical community, there has been a puzzlement concerning the broad band photoemission of interstellar dust. Within the spectra of interstellar dust atomic line spectra, there is a significant multimodal broadband emission, which has yet to be explained. Interstellar dust, composed of glassy particles with point defects, f-centers, and thermal stresses, in the presence of broadband radiation, would account for the broadband emission. (In addition, with resolution of the capture efficiencies of the incident radiation, or bringing well defined radiation (pulsed laser radiation) it should be possible to extract chemical and physical information from the interstellar dust fields, aside from rough elemental information).

Interstellar dust particles which show high internal energies, will likewise have high surface energies. These high surface energies will drive further coalescence. This eventually results in the formation of particles from micrometeorite size to planetary scale. The earth, is an interesting example. The earth is primarily composed of silicon and oxygen. These elements are in turn combined with other elements forming lower melting point species known as silicates. In fact it is fair to say that the earth is a big ball of silicates.

The earth does have a few other interesting features. The core of the earth, in spite of its age, is molten. Furthermore, it has not been possible to define a few thermal balance issues.

First, the core being molten. Many other astronomical bodies of similar age and composition to the earth are said to have solid cores. This is attributed to the earth having an anomalously slow cooling rate, the cause of which is unknown, and had pretty much been given up on.[24]

Second, the circulation of the core being largely circular, and having been spinning for some time, one would expect that the molten rock within the core would be largely be moving synchronously in a quiescent mode. It is not, in fact it is circulating roughly along its rotational axis. This might be expected if the crust of the earth were not as thick as it is, and if silicate rock were a better thermal conductor.

Third, the connection between the solar flare cycle and the planetary temperature. In a simple thermal balance model, per Einstein, under constant radiative flux, the temperature will reach equilibrium when the absorptance matches the emissivity. The total solar irradiance is roughly constant. The variation in the value for total solar irradiance for the duration of the measurement is in the order of one tenth of one percent. This is sufficiently small that there should be no global effect for a change in solar flare activity based strictly upon a solar heat flux model.

Solar flare activity has been tracked by astronomers and astrophysicists since Galileo Galilei in 1610. It has been determined that there is a relatively stable eleven year cycle from peak solar flare activity to peak solar flare activity. [25]

Curiously, there is a link between the level of peak solar flare activity and the population of arctic hares in the arctic tundra.[26] During peak solar flare activity, the population of arctic hares increases by about one thousand times. This is followed by a significant increase in the population of arctic foxes. The change in the populations of the arctic hare populations and the arctic fox populations have been tracked for over one hundred years. Further study has shown that arctic hare population is controlled by the growth rate of the vegetation in the arctic tundra. The vegetation growth rate is controlled to a large extent by the mean daily temperature. The mean daily temperature in the arctic tundra has been found to cycle with solar flare activity, seemingly independent of the total solar irradiance. The arctic tundra is one of the last locations on the planet that is virtually unaffected by human intervention. Thus, there are minimal anthropogenic effects reflected in the system. Thus, the effects are primarily due to the environmental effects upon the populations. Temperature change, vegetation growth rates, and the capability of the ecosystem to support the populations.

In the time frame of 1645 to 1715, there was a quiescent period of solar activity.[25] Solar flare activity dropped significantly. This period of sunspot inactivity is known as the Maunder Minimum. This corresponds to a climactic period called the “Little Ice Age.” During this time, rivers that are normally ice free froze and snow remained in fields year round at low altitudes.

Together, the observations of laser damaged silica, radiation damaged silica, interstellar dust, and observations of anomalous behavior of the earth, and arctic hares can provide significant insight into the behavior of radiation and matter. While very convoluted at the onset, they are all tied together by being made of atoms and molecules that interact with radiation.

Silica, and other glassy silicates, that make up much of the interstellar dust, and most of the earth, can store thermal and mechanical energy in the electron densities of the molecules from which they are composed. This is the same energy that is contained in a compressed spring, a taught string, or a stressed piece of glass. This energy in the case of silica and silicates can be up to 3.5 electron volts. It had been proposed that the maximum number of the three electron volt sites that could exist in silica was 0.05%. We have measured 70% of silica at this energy level in contamination related laser damaged. Further perturbation of the silica could result in the capability of storing more energy.

Rapidly cooled glasses and glassy materials are known to store sufficient energy to result in failure. These failures often result in propagation of the failure beyond the stressed region of the glass, this is caused by the release of the large amount of energy stored in the stress. This is commonly seen in glass art and crafts. Professional glass blowers go to extensive lengths with their work to thermally anneal these stresses out of their products. Without annealing, the lifetime of the stress in glasses is on the order of thousands of years, depending upon its environment.

From atomic and ultraviolet radiation induced damage to glasses, we know f-centers possess the same energy signature as the damage measured. These defects are frequently "photo-bleached" out using intense white light. Additionally, they lead to slow, lifetime induced relaxation, through photoluminescence. The photoluminescence spectra of these relaxations in many cases duplicates the span and distribution of the electron energy distribution seen in our laboratory. Glebov has reported that in femtosecond laser damaged glass, that two distinct photoluminescence lifetimes on the orders of microseconds and days have been measured. [23] Within our experiments it was found that the energy within a limited depth (the electron capture depth) in the silica could be extracted through low energy (0-3eV) electrons as well. The energy stored in the glass is stored in the interatomic bonds, the electronic orbitals. Thus, the thermal, mechanical, electronic, and radiation induced energy are all the same, and can be treated in any appropriate descriptive manner. We can recover the energy stored in the silica. This can be recovered at an energy levels over 3 electron volts, (300nm) within the transparent region of the silica. In extracting the energy from the silica, the stress in the silica is lowered and it is effectively annealed. Emission of photons from the point defects or stresses can stimulate the emission from other sights if they are captured by an appropriate energy level silica molecule, this molecule will likewise emit its stored energy. The result is a broadband emission as seen with interstellar dust.

Within the polar region of the planet, the magnetic fields, that protect the remainder of the planet from most of the high energy particulate radiation, do not protect the poles. This results in the impingement of a large quantity of high energy radiation at both poles. This radiation will impact the earths crust and decay from MeV and KeV to the eV range. This decay process will result in the radiation of stressed silicates in the earth. The radiation, as it passes through the earth's crust releases energy stored in the silica and silicates. Release of subsequent photons will result in multiplication of the photoluminescence yield through stimulated emission, resulting in amplification of the number of radiation events. This is amplified stimulated emission in a slightly different form. Absorption of this radiant energy into other matter will result in the decay of the energy into thermal energy, or heat. Ionizing radiation is within the energy regime of the photon emissions. This can result in the ionization of matter within the core. An event which is normally beyond the behavior of matter in a thermal equilibrium at the temperatures of the earths core.

The release of heat within the core, will add to the total heat flux of the earth, beyond the scope of the solar irradiance model. This may be related in part to the release of stored energy from materials such as silica and silicates within the earth's core. In addition, the localized heating of the molten core will result in thermal expansion and thus a localized decrease in the density of the core and thus a convective circulation of the core. As the material along the axis rises to the surface, the material toward the equatorial region will be pulled in. This with ionization of the core, will result in circular ionic movement, and its resultant magnetic field generation. The net effect would be the increase in the temperature of the earth, additional driving force for the circulation of the core and potentially an enhancement of the earth's magnetic field.

VII. Conclusions

Laser interactions with materials are not well understood. Optical damage has been modeled in a manner that makes it difficult to interrelate damage from one laser to another. The interaction of contamination with laser systems as related to optical damage effects is less well known, except in a few circumstances which are not applicable in spaceflight systems.

Spaceflight lasers offer a number of challenges not found in ground based laser systems. The sealed or vacuum atmospheres tend to accentuate damage behavior. Most terrestrial and airborne laser systems have preventive maintenance cycles during their lifetimes that are usually not an option for a spaceflight system. The preventive

maintenance provides potential recovery for failed or failing systems. Spaceflight systems are required to be: “set it launch it and forget it”. This provides little or no margin for error. As a result, spaceflight lasers are often one hundred to ten thousand times more expensive than an equivalent laboratory laser. The cost of failure for the laser in space is hundreds to thousands of times this amount.

Non-linear optical behavior has been modeled numerically making a number of assumptions that are less than reliable when working near optical damage thresholds. It is usually expected that non-linear behavior does not exist, unless it is specifically designed in or, that one is working very near laser damage thresholds. Understanding of the genesis of non-linear optical behavior from the material or atomistic level is not common. Surfaces, point defects, stress fields and contamination will greatly amplify the already present non-linear behavior within laser systems, precipitating laser induced optical damage. If laser damage were a strictly linear phenomenon that were only dependent upon average bulk behavior, the issues associated with damage in high energy laser systems would have been solved some time ago. Except in very specific circumstances other people's models work in other people's lasers. The dependence of the laser optic damage is sufficiently dependent upon laser optical properties, that the laser induced damage thresholds are only a guide.

Contamination in spaceflight lasers is inevitable. Contamination can be described much like weeds, it is something that is somewhere it is not wanted. There is always something there. You do not know ahead of time what it is, and in lasers, you will not know what the final effect is likely to be. The issues are: how much, of what, can be accepted, where. These answers are not known. Thus, the only acceptable strategy to date is to make the system free enough of contamination that at the end of mission life, a best estimate survivable limit of material could be transferred to the critical surfaces. This is usually equivalent to some number much less than one layer of molecules on the surface, to about two layers deep on the optic after years of radiation and thermal cycling. It is not impossible, but very, very expensive in terms of support facilities and manpower.

- A fundamental change was noted in laser optics damaged in the presence of laser contamination.
- There has never been a measurement showing this relationship before, and it points to a much smaller number of laser material interaction scenarios for high intensity laser induced optical damage.
- This change resulted in the differentiation of the energies of nominally identical silica molecules by a quantity on the order of three electron volts, three times the laser photon energy. This is about one third the heat of formation of silica.
- This energy is recoverable in the form of photoluminescence, at energies up into the ultraviolet.
- The energy levels seen in this silica have been noted in other silica and glass materials but at much lower concentrations.
- The photoemission of the silica could resolve the broad band emission seen in interstellar dust.
- The emission of silica could resolve the issue of the connection between arctic hare population and sun spot activity.
- The emission of the silica could resolve the issue of the anomalously slow cooling of the earth's core.
- The emission of the silica could resolve the issue of the Maunder Minimum, and the “Little Ice Age.”
- This linkage was likely not detected before due to the estimation that the maximum population density for such states was assumed to be 0.05%.
- The population density found was on the order of 3000 times this amount.
- Further, the lifetime of this state is much greater than one year under normal room conditions.

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